Cationic Platinum(II) σ-SiH Complexes in Carbon Dioxide Hydrosilation

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Dedication ((optional))

Abstract: The low electron count cationic platinum complex [Pt(I^{t}Bu')(I^{t}Bu)][BAr^F],**1**, interacts with primary and secondary silanes to form the corresponding σ-SiH complexes. According to DFT calculations the most stable coordination mode is the uncommon η^1-SiH. The reaction of **1** with Et_2SiH_2 leads to the X-ray structurally characterized 14-electron Pt^{II} species [Pt(SiEt$_2$H)(I^{t}Bu)$_2$][BAr^F], **2**, that is stabilized by an agostic interaction. Complexes **1**, **2** and the hydride [Pt(H)(I^{t}Bu)$_2$][BAr^F], **3**, catalyze the hydrosilation of CO_2 leading to the exclusive formation of the corresponding silyl formates at room temperature.

Silane σ-complexes lie at the very heart of numerous catalytic transformations.[1] Coordination of the Si−H bond of a silane to a coordinatively unsaturated metal center in either η^1-, η^2- or even η^3-fashion (Figure 1) enhances the electrophilicity at silicon making it susceptible of nucleophilic attack to form new Si−X bonds (X = O, N, C, etc), and in some cases transferring one of its hydrides to the metal atom.[2] On the other hand, isolation or even

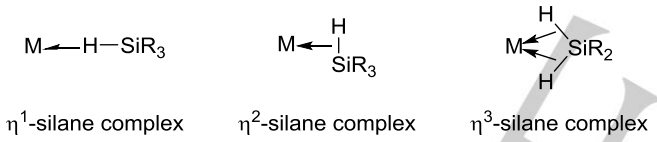

Figure 1. Coordination modes of silanes.

observation (by spectroscopic means) of silane σ-SiH species in cationic transition metal complexes is still rare,[2d,e;3] with no examples in platinum chemistry. While in most of the cases σ-SiH compounds have been formed as transient species in hydrosilation processes, and other catalytic reactions, their role in CO_2 hydrosilation have been barely studied.[4] In this sense, the catalytic reduction of carbon dioxide into more valuable compounds is gaining relevance.[5] However, its high thermodynamic stability is an important drawback. Some research groups have made use of hydrosilanes to overcome unfavorable thermodynamics in the reduction of CO_2 to formate,[4c,d;6] acetal,[7] methoxy[8] and even methane levels (Figure 2).[4a,9] Controlling the selectivity of the reaction to generate a single product is particularly challenging. Brookhart et al. reported that the iridium η^1-SiH complex [(POCOP)Ir(H)(η^1-HSiR$_3$)][B(C$_6$F$_5$)$_4$] catalyzes the conversion of CO_2 into methane.[4a] The reaction was suggested to occur through activation of the Si−H bond by the electrophilic iridium complex leading to a transient "silylium" cation that is sufficiently reactive towards CO_2. In fact, Müller and co-workers have demonstrated the role of silyl cations in the reduction of carbon dioxide.[10] Brookhart's system seems to act in part as a mere Lewis acid, in analogy to other Lewis acids based on main group elements, particularly boron.[11]

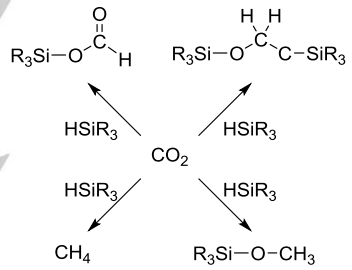

Figure 2. Possible reduction products of CO_2 with hydrosilanes.

Earlier, we have shown that the platinum(II) complex [Pt(I^{t}Bu')(I^{t}Bu)][BAr^F] **1**,[12] behaves as a highly electrophilic metal in the dehydrogenation of amine-boranes.[13] In this case, the metal is able to abstract a hydrogen atom from the borane leading to a neutral platinum species [Pt(H)(I^{t}Bu')(I^{t}Bu)] and a boronium cation, a process that takes place through the intermediacy of η^1-BH complexes. Thus, we set out to explore the reactivity of **1** towards silanes and CO_2 keeping in mind that silanes can also transfer a hydride atom in the presence of metal Lewis acids. In this communication we report the catalytic activity of formally 14-electron Pt^{II} complexes in CO_2 hydrosilation with primary and secondary silanes. The process takes place through the initial formation of Pt^{II} σ-silane complexes in which the preferred coordination mode is η^1 according to DFT calculations.

We first analyzed the interaction of silanes with complex [Pt(I^{t}Bu')(I^{t}Bu)][BAr^F], **1**, at different temperatures in an NMR tube (Scheme 1). Triethylsilane, Et_3SiH, proved to be too bulky to detect any interaction with the metal center. On the other hand, diethylsilane, Et_2SiH_2 does not show evidence for an interaction at room temperature. According to NMR data, the chemical shift of the Si−H protons in the ^{1}H NMR spectrum appeared at the same δ than in free Et_2SiH_2. However, upon cooling the solution at -60 °C, the SiH protons shifted up-field, appearing at *ca.* δ 2.20, while the signal vanished in the baseline

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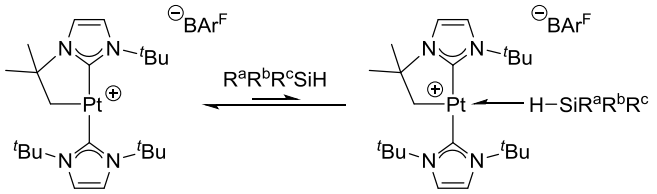
at -80 °C. This behavior is consistent with the formation of a σ-SiH platinum complex in which fast exchange between terminal



$R^a = R^b = R^c$ = Et (**1·HSiEt$_3$**);
$R^a = R^b$ = Et, R^c = H (**1·H$_2$SiEt$_2$**);
R^a = Bu, $R^b = R^c$ = H (**1·H$_3$SiBu**);
R^a = Ph, $R^b = R^c$ = H (**1·H$_3$SiPh**)

BAr^F = tetrakis[(3,5-trifluoromethyl)phenyl]borate

Scheme 1. Interaction of hydrosilanes with complex **1**.

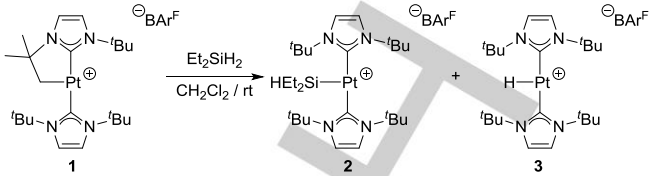
and bridging Si−H is taking place.[1b] It should be pointed out that complex **1** rearranges into a new species in the presence of Et_2SiH_2 after a few hours (see below) at rt.

When the less hindered primary silane $^nBuSiH_3$ was used, the interaction with the platinum atom at room temperature was still too weak to observe a significant change in chemical shifts and coupling constants to platinum.[14] As the temperature decreases the SiH proton signals are displaced in the ^{1}H NMR spectra to higher field as expected for formation of a σ-SiH complex. The ^{1}H−^{29}Si HMQC NMR spectrum shows a down-field shift of the resonance of the silicon atom. As a way of an example, at −50 °C the Si atom resonates at *ca.* −48 ppm, that is, 12 ppm down-field shifted with respect to the free silane (−60 ppm). The $^1J_{SiH}$ coupling constant decreases slightly on cooling (see Table S1). At lower temperatures, the fast exchange between bridging and terminal SiH protons is frozen. At -65 °C no signals for these protons are discernible whereas at the lowest temperature of the experiment (-90 °C) two broad signals centered at *ca.* 4 and -4.4 ppm with relative intensities of 2:1 are observed. The broadness of the peaks hampered observation of the corresponding coupling constants with ^{29}Si. The presence of cross-peaks between them in a NOESY experiment indicate that these two signals are undergoing exchange on the NMR time scale, thus supporting an structure as depicted in Scheme 1. Phenylsilane $PhSiH_3$ behaves in a similar way to $^nBuSiH_3$, but the dynamic exchange between terminal and bridging hydrogens was not observed even at -90 °C.

As mentioned above, complex **1** evolves cleanly into two new species in the presence of 1 equiv. Et_2SiH_2 at room temperature after a few days. These have been characterized as the low-electron count Pt^{II} silyl derivative [Pt(SiHEt$_2$)(I^{t}Bu)$_2$][BAr^F], **2** and the platinum hydride [Pt(H)(I^{t}Bu)$_2$][BAr^F], **3**,[15] (Scheme 2). The reaction can be accelerated by using a large excess (*ca.* 30 equiv) of Et_2SiH_2, which additionally results in an increase of the relative amount of the silyl complex **2** with respect to **3** (typically ~ 5%). Hydrogenation of **1**, by H_2 generated by hydrolysis of Et_2SiH_2 (catalyzed by **1**) due to the presence of adventitious water, leads to the formation of **3**. Importantly, **3** does not convert into silyl complex **2** under these experimental conditions.

On the contrary, the reaction of primary silanes $^nBuSiH_3$ and $PhSiH_3$ with **1** lead to complex reaction mixtures.

Cationic complex **2** is a rare example of a coordinatively unsaturated Pt^{II} silyl species. This type of compounds



Scheme 2. Formation of complex **2**.

has been postulated as intermediates in the generation of silylene species.[16] The SiH proton resonates in the ^{1}H NMR spectrum as a multiplet centered at 3.64 ppm coupled to ^{195}Pt ($^2J_{Pt,H}$ = 115 Hz) consistent with the formulation of **2** as a platinum silyl species.[17] The ^{1}H,^{29}Si -HMQC NMR spectrum shows a signal at 18.1 ppm for the silyl group. These experimental observations were further borne out by X-ray diffraction studies (Figure 3), which show the platinum atom surrounded by two I^{t}Bu ligands in a mutually *trans* disposition and a silyl fragment with no ligand *trans* to it. One of the CH bonds of a *tert*-butyl group is in close proximity to the metal center (Pt···H9a and Pt···C9 distances of 2.206(1) and 2.950(1) Å), suggesting that an agostic interaction is stabilizing the highly electrophilic platinum atom. The angle defined by the two carbenes and the platinum atom (C1−Pt1−C12) deviates from linearity (167.4(3)°) as a consequence of the buttressing effect of the silyl ligand exerted on the NHC that stablishes the agostic interaction. The Pt1−Si1 bond distance of 2.314(3) Å falls in the expected region for Pt^{II} silyl species.

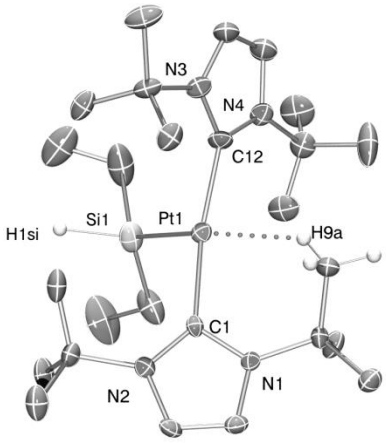


Figure 3. Molecular structure of complex **2** determined by X-ray crystallography. BAr^F anion and most of hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 30% probability.

At variance with hydride **3** that was not possible to be isolated in the solid state due to its propensity reform **1**, cyclometalation of **2** with concomitant extrusion of Et_2SiH_2 takes place at rt (25% of conversion after 5 days) or under mild heating for a few hours. On the other hand compound **2** does not react with H_2 leading to Et_2SiH_2 and **3** which contrast with the fast hydrogenation of the cyclometalated species **1**.

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The interaction of $^{n}BuSiH_3$ and Et_2SiH_2 with silyl and hydrido derivatives **2** and **3** was also explored. VT NMR studies have proven that formation of their σ-SiH complexes is less favored than in the case of **1**. For example, ^{1}H NMR spectra of the silyl species $[Pt(SiEt_2H)(I^tBu)_2][BAr^F]$ in the presence of 1 equiv of $^{n}BuSiH_3$ shows only a marginally different chemical shift of the SiH_3 protons at −90 °C (0.1 ppm downfield shifted with respect to the ^{1}H NMR spectrum recorded at rt). Expectedly, the silicon nucleus of $^{n}BuSiH_3$ resonates in the ^{29}Si NMR spectra at *ca*. −58 ppm). Similarly, negligible interaction is observed in the case of hydride $[Pt(H)(I^tBu)_2][BAr^F]$ and Et_2SiH_2 (SiH protons of Et_2SiH_2 0.2 ppm downfield shifted with respect to the ^{1}H NMR spectrum recorded at rt).

All attempts to obtain crystals suitable for X-ray diffraction for the σ-SiH complexes at low temperature failed. Thus, we turned to DFT calculations ((M06/6-31g(d,p) + SDD; see ESI)[18] to analyze the stability and coordination mode of the silanes to complexes **1**-**3** (Figure 4). According to the calculations, coordination of the silane molecules to complexes **1**-**3** in a σ-SiH fashion is exothermic in all cases with energy returns in the range -12.8 to -8.2 kcal·mol^{-1} (Table S8), which lays within the expected loss of entropy at r.t.,[19] and agrees with coordination of the silanes to the metal complexes at temperatures lower than room temperature. Also, the calculations predict a slight preference for the coordination of Et_2SiH_2 to all metal fragments and, in agreement with our observations, of both silanes to **1**.

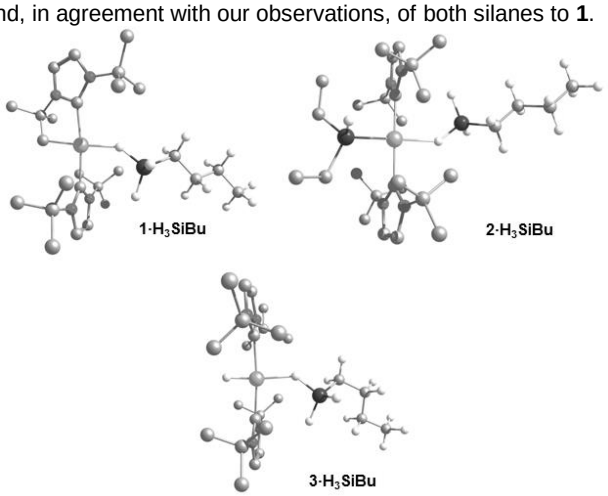


Figure 4. DFT calculated structures of complexes **1**-**3**·**H$_3$SiBu.**

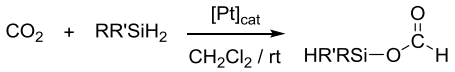
The Pt···Si distances (greater than the sum of the covalent radii) and Pt···H−Si angles are consistent with a preferred η^1-Si−H coordination mode,[2d] but some differences in the structural parameters have been observed (Table 1). Complex **1** is the one that forces to a greater extent the η^1 coordination mode according to the angle defined by the Pt···H−Si atoms and the Pt···Si bond distances (Table 1). This is likely due to the cyclometalated nature of the NHC that, at variance to the non-cyclometalated I^{t}Bu ligands in complexes **2** and **3**, cannot rotate about the Pt−C$_{(carbene)}$ bond to accommodate the silane. The Pt···H and Pt···Si distances in complexes **2**·**H$_3$SiBu** and **2**·**H$_2$SiEt$_2$** are considerably longer (see Table 1). A closer look at the angles defined by the two carbene carbon atoms and the platinum center hints at a possible explanation. These angles are nearly 182° for these species, compared to the *ca*. 175° in **3**·**H$_3$SiBu** and **3**·**H$_2$SiEt$_2$**, that is, the Et_2SiH fragment in complexes **2**·**H$_3$SiBu** and **2**·**H$_2$SiEt$_2$** is pushing the I^{t}Bu ligands towards the silane, hampering its interaction with the platinum atom. Obviously, the C$_{(carbene)}$−Pt−C$_{(carbene)}$ angles in the

Table 1. Selected structural parameters of the DFT-optimized geometries for the silane adducts.

Complex[a]	Pt···H(Å)	Pt···Si(Å)	Si···H(Å)	Pt−H−Si(°)	C−Pt−C(°)
1·H$_3$SiBu	1.96	3.33	1.53	145.25	173.28
2·H$_3$SiBu	2.24	3.54	1.51	140.73	182.52
3·H$_3$SiBu	1.95	3.24	1.53	137.09	174.75
1·H$_2$SiEt$_2$	1.96	3.44	1.53	159.07	171.46
2·H$_2$SiEt$_2$	2.18	3.63	1.52	157.25	182.35
3·H$_2$SiEt$_2$	1.94	3.39	1.53	154.81	175.45

analogous **1**·**H$_3$SiBu** and **1**·**H$_2$SiEt$_2$** species are enforced to be more acute, but the coplanar disposition of the cyclometalated NHC ring (with respect to the coordination plane of the platinum atom) orientate the ^{t}Bu group towards the silane. As expected, the NBO analysis (see ESI) indicates the increase in partial positive charge on the silicon atom upon stablishing an interaction with the metal center.

The close relationship of these Pt^{II} σ-SiH complexes and the Ir^{III} species reported by Brookhart, prompted us to study the catalytic activity of derivatives **1**-**3** in CO_2 hydrosilation (Scheme 3). Although these complexes are inert in the presence of CO_2,[20] catalytic activity was observed in mixtures of silanes and CO_2. Complex **1** proved to be the most efficient of the three, while **2** and **3** are quite comparable. When catalyst **1** (0.5 %) was reacted with $^{n}BuSiH_3$ under 5 atm of CO_2, a clean reaction took place leading almost exclusively to silylformate $^{n}BuSiH_2(OCOH)$ in *ca*. 15 min at room temperature quantitatively (by NMR). The TON and TOF numbers associated with this transformation are 200 and 714 h^{-1} (Table S2).



R = H, R' = ^{n}Bu; R = R' = Et

Scheme 3. Hydrosilation of CO_2 catalyzed by complexes **1**-**3**.

This result is in stark contrast with the reduction of CO_2 using trialkylsilanes catalyzed by the iridium complex $[(POCOP)Ir(H)(\eta^1\text{-}HSiR_3)]^+$, for which over-reduction to methane was observed, but resembles pretty much that observed by Chen *et al.* with the aluminium Lewis acid $Al(C_6F_5)_3$ in the absence of $B(C_6F_5)_3$ as co-catalyst.[9a] The selectivity of the process towards the monoformate is also remarkable. In spite of the limited studies on the reduction of CO_2 by primary silanes, incorporation of two or even three molecules of carbon dioxide leading to bis- and tris-formates is prevalent in most of the

cases.[6a,g]. On the other hand, under the same catalytic conditions, complexes **2** and **3** (0.5%) required 10 h to fully convert $^{n}BuSiH_3$ into silyl-formate $^{n}BuSiH_2(OCOH)$. At the end of these catalytic reactions, catalysts **2** and **3** remained intact, while catalyst **1** was partially transformed into hydride **3** due to the presence of adventitious water.

$PhSiH_3$ was also used for the hydrosilylation of CO_2. However, in spite of the presence of silylformate compounds, several other unidentified products were produced.

Et_2SiH_2 does also generate the corresponding silylformate $Et_2SiH(OCOH)$ with catalyst **1**. Nevertheless, the reaction proceeded at considerably slower rates in comparison with the reactions carried out with butylsilane and, in addition, higher catalyst loadings (3%) were required to achieve full conversion after 6h at rt. Once more, we have noticed that hydrolysis of Et_2SiH_2 with release of H_2 is detrimental for the catalytic activity of complex **1** due to formation of the less catalytically active complex **3**. Likewise, complexes **2** and **3** catalyzed the transformation of Et_2SiH_2 into $Et_2SiH(OCOH)$ but very long reaction times were necessary (see Table S2).

In summary, we have detected by NMR the formation of silane σ-complexes with the highly electrophilic platinum complex **1**. According to DFT calculations, the most favored coordination mode is the rare η^1-SiH for which only one example has been reported. In one of the cases, the coordination of the silane precedes the Si−H bond cleavage leading to the first structurally characterized cationic Pt^{II}-silyl complex $[Pt(SiHEt_2)(I^tBu)_2][BAr^F]$, **2**. The interaction of the silanes with the platinum atom depends strongly on the orientation of the NHC with respect to the metal center, being more favored when is cyclometalated. The enhanced electrophilicity of the silicon atom in the silane through its coordination to platinum (in a similar way than the iridium complex reported by Brookhart) makes it reactive enough to hydrosilate CO_2 in a selective way towards mono-silylformates. Ongoing efforts are geared toward crystallographical characterization of a σ-SiH platinum complex and understanding the mechanism for the hydrosilation of CO_2.

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Keywords: Platinum • Carbon Dioxide • Silane • σ-complex • Hydrosilation

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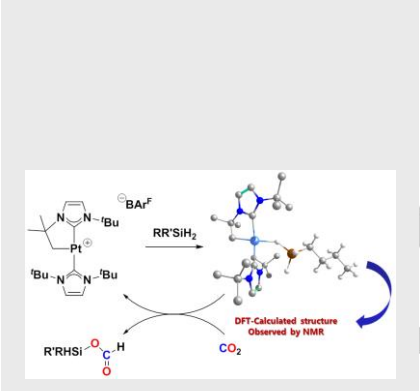

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